

PATENT ABSTRACTS OF JAPAN

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(54) PRODUCTION OF CHEMICAL REINFORCEMENT-TREATED GLASS AND ITS USE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a glass excellent in breaking strength and chemical resistance and useful as a glass substrate for hard disks, by subjecting a glass of a specified composition to a specific chemical reinforcement treatment.

SOLUTION: This glass is obtained by subjecting a glass with the composition described below to such chemical reinforcement treatment as to be 0.5-20h in immersion time at 350-550° C in an ion exchange bath containing >90wt.% of a potassium salt (e.g. KNO₃). The composition is as follows (on an oxide basis): SiO₂: 63.0-67.5mol%, Al₂O₃: 9.5-12.0mol%, Na₂O: 8.5-15.5mol%, K₂O: 2.5-4.0mol%, MgO: 3.0-9.0mol%, Σ CaO+SrO+BaO+ZnO: 0-2.5mol%, TiO₂: 0.5-1.5mol%, CeO₂: 0.02-0.5mol%, As₂O₃: 0-0.35mol%, SnO₂: 0-1.0mol%, F₂: 0.05-2.6mol%, under the following conditions: SiO₂/Al₂O₃=5.3-6.85, Na₂O/K₂O=3.0-5.6, Al₂O₃/K₂O=2.8-3.6, Al₂O₃/(TiO₂+CeO₂)=7.6-18.5.

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CLAIMS

[Claim(s)]

[Claim 1] The presentation SiO₂ of the following [oxide criteria] 63.0-67.5-mol %, aluminum 2O₃ 9.5-12.0-mol % and Na₂ O 8.5-15.5-mol % and K₂ O 2.5-4.0-mol %, MgO 3.0-9.0-mol %, sigma CaO+SrO+BaO+ZnO 0-2.5-mol %, TiO₂ 0.5-1.5-mol %, CeO₂ 0.02-0.5-mol %, As 2O₃ 0-0.35-mol %, SnO₂ 0-1.0-mol % and F₂ 0.05-2.6-mol % — however — SiO₂/aluminum₂ O₃ 35.3-6.85 Na₂ O/K₂ O 3.0-5.6 K₂ O [aluminum₂ O₃/] 2.8-3.6 aluminum₂ O₃/(TiO₂+CeO₂) In the ion-exchange bath which contains more potassium salt than 90 % of the weight in the glass which has 7.6-18.5 The manufacture approach of the glass by which chemical-strengthening processing was carried out of reaching in the high fracture strength characterized by performing chemical-strengthening processing over 0.5 - 20-hour immersion time amount at the temperature of 350-550 degrees C, and having high chemical resistance.

[Claim 2] the glass to be used — As 2O₃ And SnO₂ at least one sort of components chosen from the becoming group — at least 0.02-mol % — approach according to claim 1 characterized by containing.

[Claim 3] The approach according to claim 1 or 2 that the glass to be used is characterized by containing 0.02-0.35-mol % of As 2O₃.

[Claim 4] An approach given in claim 1 characterized by grinding glass after chemical-strengthening processing thru/or any 1 term of 3.

[Claim 5] Use as a glass substrate for hard disks of the glass manufactured according to the approach of a publication in claim 1 thru/or any 1 term of 4.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Fracture strength of this invention is high and it is related with the manufacture approach of the glass by which chemical-strengthening processing (chemical reserve stress grant processing) was carried out excellent also in chemical resistance, and use of such glass.

[0002]

[Description of the Prior Art] Since glass is divided and has the property of low surface roughness and smooth nature which should be mentioned especially as compared with a metal like aluminum or various metal alloys, when using it as a substrate of a data-hold medium (hard disk), it is advantageous. Such glass for substrates needs to bear the heavy load added chemically, thermally, and mechanically at the time of the inside of manufacture of a hard disk, or use. That is, such glass is heated by the elevated temperature between coatings (for example, based on cathode sputtering), and is cooled after that for a short time. The big mechanical load also at the time of the use as a hard disk — starting — such a load — for example, rotational speed — 3,500 – 10,000rpm and the bolting stress to a revolving shaft — 300N/mm² **** — it becomes.

[0003] The glass which has not performed strengthening processing will be fractured very easily, if a tensile stress is added. Especially, in the case of thin glass with a thickness of 0.25–3.00mm, a load which was mentioned above only when strengthening processing (reserve stress grant processing) was carried out can be borne. Compared with the glass which has not performed strengthening processing, a load with it is added, and the glass which has performed strengthening processing becomes comparable [the probability of fracture] for the first time. [the low namely, probability fractured also by the predetermined load and] [bigger]

[0004] Since 3mm or more in thickness is needed also at the lowest in order to increase a mechanical strength by heat strengthening (thermal reserve stress grant), the chemical strengthening by the ion exchange in the inside of a salt bath serves as alternative here. In the chemical strengthening of a under from a glass transition point T_g, alkali-metal ion with the small ion diameter in glass is permuted by alkali-metal ion with the big ion diameter in a salt bath, for example, it is Li⁺. Na⁺ Na⁺ K⁺ It permutes. about [consequently, / of the ion-exchange depth] — a compressive-stress band with a thickness [equivalent to two thirds] of about 14–230 micrometers forms — having — 350–900N/mm² Bending strength is attained.

[0005] One important factor which will be accepted when generating a compressive-stress layer well is the presentation of glass. If Li ion exists in glass, it will become difficult to advance an ion-exchange process. The ion exchange [this / Li⁺] of two types, i.e., it is, Na⁺ The permutation to depend and Na⁺ K⁺ It is because the permutation to depend will arise and it is usually necessary to observe the specific mixing ratio of Na salt and K salt, and a narrow temperature requirement in process of the ion exchange. With oxygen ion, the fluoride in glass forms the anion network structure of glass, and can also diffuse big ion easily in such network structure. This will promote reduction of stress. When substrate glass contains comparatively a lot of fluorides, a chemical strengthening is usually the process of whether only a short period of time is attained and coating, for example, either of whether it will be almost lost at the time of heating. The quality of glass concerning the number and size of a defect of solid inclusion, a bubble, etc. at the above mentioned application is also important. This is because a concave hole will arise at the time of polish and the irregularity which cannot be permitted on a front face will arise, if air bubbles are shown in a substrate front face.

[0006] German patent application public presentation official report DE 42 06 268 The lithium content aluminosilicate glass for hard disk substrate glass is indicated by aluminum number. LiO₂ Although ***** is improved by existing, a chemical strengthening also becomes difficult for coincidence. In addition to surface smooth nature with a glass substrate, chemical resistance is also very important for the functionality of a fixed disk. In order to locate reading / writing head of a computer in the point-blank range of about 50nm and to function convenient from the hard disk which is carrying out high-speed rotation, this distance needs to be held correctly. However, resistance does not have the substrate front face of a hard disk to an operation of atmospheric air, and if a front face is ruined (for example, efflorescence), or adhesive strength with each class by which a front face is ****(ed) on a front face for an operation of atmospheric air is lost and exfoliation arises by the attack of a chemical before a coating activity, the distance of a head and a disk will decrease.

[0007] It is also a problem that the resistance on the front face of glass to water, caustic alkali liquid, or an acid usually decreases by chemical-strengthening processing, i.e., increase of the concentration of comparatively big alkali-metal ion. Not only chemical resistance falls, but [when alkali-metal concentration rises] this is for the attack operation by the chemical to increase, so that alkali-metal ion is large.

[0008] The purpose of this invention is to offer the manufacture approach of the chemically strengthened glass which is excellent also in chemical resistance and bending strength is not only high, but can be especially used suitably as a substrate for hard disks.

[0009]

[Means for Solving the Problem] In order to attain said purpose, according to this invention, the presentation SiO₂ of the following [oxide criteria] 63.0–67.5–mol %, aluminum 2O₃ 9.5–12.0–mol % and Na₂ O 8.5–15.5–mol % and K₂ O 2.5–4.0–mol %, MgO 3.0–9.0–mol %, sigma CaO+SrO+BaO+ZnO 0–2.5–mol %, TiO₂ 0.5–1.5–mol %, CeO₂ 0.02–0.5–mol %, As₂ O₃ 0–0.35–mol %, SnO₂ 0–1.0–mol % and F₂ 0.05–2.6–mol % — however — SiO₂/aluminum₂ O₃ 3.3–6.85 Na₂ O/K₂ O 3.0–5.6 K₂ O [aluminum₂ O₃/] 2.8–3.6 aluminum₂ O₃/(TiO₂+CeO₂) In the ion-exchange bath which contains more potassium salt than 90 % of the weight in the glass which has 7.6–18.5 The manufacture approach of chemically strengthened glass of reaching in the high fracture strength characterized by performing chemical-strengthening processing over 0.5 – 20-hour immersion time amount at the temperature of 350–550 degrees

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C, and having high chemical resistance is offered.

[0010]

[Embodiment of the Invention] The requirements for making the compressive-stress band which has a desired property generate at a strengthening (reserve stress grant) process are the presentations of glass. With the aluminosilicate glass used by this invention, it is SiO₂. It is because the melting point will rise superfluously if a content must not exceed 67.5-mol % and this exceeds this content. On the other hand, it is SiO₂. Even if a content becomes less than [63.0 mol %], it does not become, but this is because chemical resistance is spoiled remarkably under in this content. aluminum 2O₃ since it is the same A content must not exceed 12.0-mol %, either and must not be less than [9.5 mol %], either. It is SiO₂ in order to secure the both sides of good acid resistance and good ion-exchange nature. aluminum 2O₃ It is necessary to exist by the ratio which was able to take balance mutually. Namely, SiO₂ / aluminum 2O₃ There must be a mole ratio within the limits of 5.3-6.85.

[0011] There is an alkali-metal oxide as a fundamental component of glass. By combining effectively the clarifier mentioned later according to this invention, it becomes possible to except Li₂ O completely, and it becomes possible to attain a desired property to coincidence about the both sides of surface quality and a chemical strengthening with single glass. There must be a Na₂ O content in 8.5-15.5-mol% of within the limits. By chemical resistance falling, if a Na₂ O content exceeds 15.5-mol %, if lower on the other hand than 8.5-mol %, it will be hard coming to fuse glass in the first place first, and it is Na⁺/K⁺ to the second. The increment in the reinforcement only by the ion exchange will be restricted.

[0012] The component which has an exceptional and surprising operation is K₂ O, and this component needs to exist in % of the amount of 2.5-4.0 mols. This component increases the melting nature of glass and promotes the ion-exchange process by K ion in a salt bath of Na ion in glass. Furthermore, a homogenization process is also simplified and it also becomes approaching the condition of request that a bubble is absent. This is for simplifying ****, without spoiling the chemical resistance and chemical-strengthening nature (chemical reserve stress grant nature) which the direction of K₂ O increased the basicity of glass, consequently were excellent compared with Na₂ O of the number of the said mols. It is only the case of above-mentioned within the limits that same chemical and the glass which has a mechanical property and was excellent in the cellular property can be manufactured easily. Less than [2.5 mol %], when the ratio of aluminum₂ O₃ / K₂ O is less than 2.8, the content of K₂ O The consistency of air bubbles and the size of air bubbles increase, and on the other hand, the content of K₂ O is larger than 4.0-mol %, and when the ratio of aluminum₂ O₃ / K₂ O is larger than 3.6, reinforcement of glass cannot be enough increased between chemical-strengthening processings (chemical reserve stress grant processing). Two sorts of alkali-metal oxides also need to exist by the ratio which was able to take balance mutually. That is, there must be a mole ratio of Na₂ O/K₂ O within the limits of 3.0-5.6.

[0013] other indispensable components — MgO — it is — the minimum — 3.0-mol % — it is necessary to exist Consequently, the basicity of glass rises and homogenization is promoted. However, under existence of bivalence ion, since Na ion joins together more strongly in aluminosilicate glass structure, MgO is also checking an ion-exchange process. For this reason, MgO must not exceed 9.0-mol % at the maximum. Other alkaline-earth-metal oxides and ZnO also have the same operation. therefore, this glass — CaO, SrO, BaO, and ZnO — total amount sigma CaO+SrO+BaO+ZnO — it is — 0-2.5-mol % — it can contain 0.1 to 2.5% preferably. The thing with MgO more desirable than other alkaline-earth-metal oxides and ZnO is because there are few degrees which spoil chemical resistance than these oxides, while MgO raises melting nature like BaO and CaO. Furthermore, it is TiO₂. It is the indispensable component of glass. TiO₂ 1.5-mol% of that whose content needs to be more than 0.5 mol % — it must not exceed — this — this — it is because trouble arises between melting of a batch that it is out of range.

[0014] In order to obtain the best result about a bubble property, other components, i.e., clarifier, and founding assistants also need to exist in the combination which was able to take balance. Glass is CeO₂ of % of the amount of 0.02-0.5 mols. It is necessary to contain. CeO₂ It not only has a founding function, but it gives the absorbing power of ultraviolet rays with many medicine top problems high enough to glass. Therefore, use of the glass in lighting industry also becomes possible. The initial complement of a clarifier is aluminum 2O₃ which exists in glass. Being influenced by the amount was found out. aluminum 2O₃ which exists in glass The initial complement of a clarifier increases, so that there are many amounts. It is necessary to make it the mole ratio of aluminum₂ O₃/(CeO₂+TiO₂) specifically become within the limits of 7.6-18.5. As other clarifiers, it is As₂ O₃ not more than 0.35 mol %. And SnO₂ not more than 1.0 mol % It is suitable. It is desirable that at least one side recognizes amount existence beyond 0.02 mol % among two sorts of these components. The glass used in the semantics [there are few bubbles and] that size is small especially in order to be quality is As₂ O₃ of % of the amount of 0.02-0.35 mols. It is necessary to contain.

[0015] Glass is F₂ of % of the amount of 0.05-2.6 mols further. It is necessary to contain. The minimum of this range is set up on the need for cellular quality, and an upper limit is set up in view of the above-mentioned operation of the fluoride to the network structure of glass. In the case of arsenic content glass, it is F₂ [0.05-0.7 mol %]. F₂ which is 0.5-2.6-mol % when a content is desirable and is arsenic non-containing glass A content is desirable.

[0016] It is possible to create simply the compressive-stress band of high depth which compressive stress maintains over a long period of time according to a chemical strengthening with such glass to a surprising thing, without spoiling the good chemical resistance. 100 % of the weight - 90% of the weight or more of potassium salt is contained, and glass goods are immersed in a salt bath [as / whenever / bath temperature / whose / is 350-550 degrees C] over 0.5 - 20 hours. By such processing, a compressive-stress band about 14 to 230 micrometers or more generates [thickness]. The immersion time amount of long duration is needed, so that temperature is low in that case. All things the anion is stable in the above-mentioned temperature requirement can be used for a salt bath by general potassium salt. A potassium content reduces a salt bath (it usually starts from 100% of potassium salt) for the ion exchange, and when the desired ion-exchange depth is no longer obtained, they are exchanged. It is usually a time of potassium salt becoming 90 % of the weight to become such a situation. It is also possible to use 10 or less % of the weight of other salts, and to lower the melting point of a bath from the beginning. It means that the ion-exchange capacity of a bath exhausts this the part earliness, of course.

[0017] When the ion exchange performs a chemical strengthening on glass, a result whose front face is ruined depending on the case may be brought. In the advantageous embodiment of the new approach of this invention, glass is ground after strengthening. The compressive-stress layer from which it is obtained by this invention that such a series of down stream processing from which the conventional technique differs can be performed is because it is thick, without spoiling the fracture strength excellent in this invention. Although it is desirable to carry out to 25 micrometers or more in thickness and it performs the ion exchange over about 1 hour for that purpose at the temperature of 450 degrees C, as shown in Table 2, even if other processing times and temperature are used for a compressive-stress layer, it is possible for considering as such thickness. If it grinds after strengthening, the glass which has the surface characteristic which could remove again mechanical change produced on the front face, and was excellent

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between chemical-strengthening processings can be obtained, and, moreover, good chemical resistance will also be maintained. If the approach of this invention is used, since a surface characteristic not only improves, but a **** process can be reduced, the manufacture approach will also be simplified. Polish of glass is performed using cerium oxide and it is made for granularity to be set to less than 1nm with an RMS value (mean square value).

[0018]

[Effect of the Invention] The advantage of the new approach of this invention is as follows. That is, the tempered glass manufactured by the approach of this invention has the following properties, and this is a combination peculiar to this invention.
 - High bending strength, - A deep compressive-stress band, - That the generated compressive stress does not ease substantially,
 - Good surface quality and - High chemical resistance.

Since the tempered glass manufactured by the new approach of this invention has the peculiar property, it is the best for using it as substrate glass for hard disks. Probably, other effectiveness and advantages of this invention will be clear from the above mentioned explanation and the following examples.

[0019]

[Example] Table 1 shows some examples of the tempered glass manufactured by the new approach of this invention, and is those presentations and KNO₃. The ion-exchange conditions of a under [a bath], chemical resistance, and many properties relevant to strength are shown.

[0020] Glass was manufactured from the usual raw material in the platinum crucible containing 4l. The raw material was supplied over 8 hours with the melting temperature of 1,580 degrees C. After holding glass to this temperature over 14 hours after that, it cooled to 1,400 degrees C over 8 hours, stirring, and it was poured out in the mold of the graphite which carried out remaining heat to 500 degrees C. In order to conduct a preliminary visual inspection, this casting block was processed into tubing which ground the front face. The glass board to which the circular glass board which has the configuration and dimension of a hard disk substrate, i.e., an outer diameter, was [the hole with a diameter of 20.0mm] thick in 65.0mm by the usual approach, and it was thick in the center in 0.635mm from this casting block was manufactured. It is KNO₃ to grinding and this ground glass board in a precision. Chemical-strengthening processing was performed under the monograph affair shown in the table in the bath.

[0021] Each property and parameter which were shown all over Table 1 are measured using the following physical analysis. Bending strength is measured by the approach of the following usually used in glass industry, and aims at the load produced in actual use. What was performed is the so-called duplex ring trial, and in this trial, a diameter lays it on the metal support ring which has the annular cutter of hardening steel with a diameter somewhat smaller than 60mm (ϕ = 65mm), i.e., the test objective glass board, in the chemical-strengthening processing glass board which has the configuration and dimension of a hard disk substrate, and it doubles a core. On this glass board, another metal support ring which has a steel cutter is laid similarly, and a core is doubled. A diameter is 25mm and this cutter has a diameter somewhat larger a little than the hole (ϕ = 20mm) of the center of a hard disk substrate. Push, therefore a hard disk substrate will be joined the rate for 2mm/by the force which continues increasing with constant speed in the glass board by which the cutter of the ring by the side of besides was laid on the cutter of a lower ring. Let the load in the time of a substrate fracturing be bending strength (N/mm²). In this trial, a load regards it as success, when fracture arises for the first time exceeding 100 Ns.

[0022] Compressive stress is measured by the stress-optical method. That is, when compressive stress has joined the glass plate, change arises in the refractive index of an parallel and perpendicular direction to the stress direction, and a glass plate comes to show a birefringence. The birefringence, i.e., the difference of these refractive indexes, is proportional to the added stress according to the stress-optical multiplier of the glass concerned, and it is measured from the optical path difference after the reflection in respect of the glass of a perpendicular and parallel polarization light.

[0023] The thickness of a compressive-stress band is the following, and is made and measured. A glass sample is observed on the wavelength of 546nm by the bottom of a polarization microscope. From the reasons of a balance, compressive stress has joined all front faces and, as for the sample to which the ion exchange was given, the tensile stress has joined the interior. In order to measure stress, a sample is placed between two polarizers made to cross. The stress which has joined the sample produces brightness in stress double refraction, therefore the optical path of a microscope. The transition (zero-order neutral band) to compressive stress from a tensile stress is visible clearly as a dark-colored broadcloth band under a microscope. The distance from a sample edge to a zero-order band serves as measured value of the thickness of a compressive-stress band. Since the above-mentioned glass board was too thin for performing this measurement, it used the piece of glass which was manufactured and hardened on the same conditions as this glass board and whose thickness is 2mm in 6mmx50mm for this measurement.

[0024] Knoop hardness is measured according to DIN52333. The quick and simple test method which used easy equipment is indispensable to chemical-resistant measurement. There is no standard test method which specialized in the glass data-hold medium despite today. Although various kinds of test methods which investigate the chemical resistance of glassware are known for glass industry, those approaches are unsuitable although the chemical resistance of a hard disk substrate is judged by various reasons.

[0025] The so-called amount of alkali extraction of the disk manufactured by the new approach of this invention can be carried out simple, and is judged by the new approach to obtain a very significant result. Here, vocabulary called the amount of alkali extraction shall mean the total amount of the alkali-metal ion eluted from a sample in the following trial carried out on condition that the following. The glass disk [finishing / strengthening processing] which has an above-mentioned configuration and an above-mentioned dimension, i.e., an outer diameter, is 65.0mm, a sample is the glass board with a thickness of 0.635mm to which the hole with a diameter of 20.00mm opened in the center, an edge picks grinding and a field to a precision, and a front face is ground until it serves as less than 1nm of RMS roughness using cerium oxide. With the condition of having washed and having become wet with the last washing process over 1 / 4 hours at the room temperature in the ultrasonic bath using deionized water, the sample which performed strengthening processing, or the sample which performed strengthening processing and polish in the suitable embodiment was immersed into 25ml of 80-degree C deionized water, and was left as it was for 24 hours. The amount of the alkali-metal ion which exuded was measured by atomic absorption analysis. The amount (mg) of the alkali metal which exuded in each example is a thing about one sample respectively.

[0026]

[Table 1]

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本発明の新規な方法によって製造した強化ガラスの組成 (モル%、酸化物基準) 及びその本質的特性							
実施例No.	1	2	3	4	5	6	7
SiO ₂	65.54	67.32	63.60	63.67	66.26	66.83	67.36
Al ₂ O ₃	9.60	11.18	11.91	9.74	10.91	10.91	11.28
Na ₂ O	8.66	13.58	12.49	16.02	11.30	11.30	12.82
K ₂ O	2.68	3.17	3.48	2.89	3.82	3.82	3.82
MgO	8.62	3.29	6.51	3.97	3.25	3.25	3.25
CaO + SrO + BaO + ZnO	1.25	0.24	0.47	0.14	0.12	0.12	0.24
SnO ₂	1.0	—	—	0.15	—	—	0.15
TiO ₂	1.19	0.54	0.66	0.64	1.23	0.66	0.54
CeO ₂	0.06	0.46	0.02	0.15	0.19	0.19	0.15
F ₂	1.41	0.09	0.51	2.53	2.59	2.59	0.22
As ₂ O ₃	—	0.17	0.35	0.05	0.33	0.33	0.17
イ ⁺ 交換温度 (°C)	500	450	400	450	480	480	520
イ ⁺ 交換時間 (時間)	10	1.5	5	4	6	6	20
圧縮応力帯域の厚さ (μm)	105	35	45	52	128	125	220
7M ⁺ 金属の浸出量 (μg)	21	20	24	22	18	23	17
300 °Cでの「応力緩和」 (h)	950	>1000	>1000	700	800	850	>1000
曲げ強さ (N/mm ²)	720	490	410	560	640	620	900
メ ⁺ 硬度 (KH)	585	590	600	545	562	568	609
弾性率E (kN/mm ²)	70	71	72	66	68	68	72
熱膨張係数 α _{20/300} (10 ⁻⁶ /K)	8.2	8.9	9.1	9.6	9.1	9.1	8.9
ガラス 遷移温度T _g	595	632	616	565	573	579	626

The amount of extraction of alkali metal means the total amount of extraction of the alkali-metal ion per hard disk substrate at the time of performing an above-mentioned trial under above-mentioned conditions (μg). Rhine of "stress relaxation (h)" shows the time amount (h) taken to decrease until the thickness of a compressive-stress band becomes measurable, when it is made into constant temperature (300 degrees C). Incidentally, change of the thickness which exceeds 4 micrometers is measurable. It is as having already explained the used optical means. Such reduction of the thickness of a compressive-stress band is easier to measure than compressive-stress relaxation itself in relation to reduction of compressive stress.

[0027] KNO₃ In the bath, while carrying out chemistry hardening of the glass which has the presentation of the example 3 of Table 1, ion-exchange time amount was changed from 1 / 2 hours to 15 hours, and whenever [bath temperature] was changed from 350 degrees C to 550 degrees C. The thickness (micrometer) of the obtained compressive-stress band is shown in Table 2. The range of the thickness of a compressive-stress band was 14-230 micrometers, and the point which needs such long immersion time amount that temperature is low was as prediction.

[Table 2]

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表 1 の実施例 3 の組成を有するガラスについての、イオン交換時間又は塩浴温度の関数としての圧縮応力帯域 (μm)					
イオン交換時間 (h)	浴温度 ($^{\circ}\text{C}$)				
	350	400	450	500	550
0.5		14	20	38	46
1			26	55	68
1.5		20	30	60	90
2.5		31			
4			42		121
5		45		98	
8			75		
10		63	90	132	182
15	47	72	103	165	230

[0028] Thus, it depends for the thickness of a compressive-stress band to ion-exchange time amount (when ion-exchange temperature is fixed) and the both sides of ion-exchange temperature (when ion-exchange time amount is fixed) clearly. Table 3 shows that it is certainly applied about bending strength, although such a dependency is not applied to the compressive stress in a front face as it is. What was chosen as operation glass also in this case was glass which has the presentation of the example 3 of Table 1.

[Table 3]

表 1 の実施例 3 の組成を有するガラスについての、一定の塩浴温度 (450 $^{\circ}\text{C}$) でのイオン交換時間の関数としての圧縮応力帯域の厚さ、表面での圧縮応力、及び曲げ強さ			
イオン交換時間 (h)	圧縮応力帯域 の厚さ (μm)	表面での圧縮 応力 (N/mm^2)	曲げ強さ (N/mm^2)
1.5	30	880 ± 30	430
15	103	775 ± 30	800

Since it has the value of the above very good bending strength, the tempered glass manufactured by the new approach of this invention is the optimal when bearing the mechanical load by which the current load is carried out to the hard disk (high speed of a future hard disk), or a load will be carried out to it.

[0029] The temperature dependence of the stress relaxation which made reference in relation to the above-mentioned table 1 is shown in Table 4. It is the hard disk substrate manufactured for this purpose from the glass which has the presentation of the example 7 of Table 1 KNO_3 It was made to harden over 20 hours in a bath at 520 degrees C. Compressive stress is 2800Ns/mm. The compressive-stress band which is 220 micrometers was formed. Table 4 is each temperature and shows the time amount which passed by the time reduction of the thickness of a compressive-stress band was observed.

[Table 4]

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表 1 の実施例 7 の組成を有するガラスについての、所定温度で圧縮応力帯域の厚さに測定可能な減少 ($4\mu\text{m}$) が生じるまで経過した時間

温度 ($^{\circ}\text{C}$)	時間 (h)
300	> 1000
350	500
400	100
500	30

If it extrapolates, by the time stress relaxation arises, 50,000 hours or more will pass at the temperature of 200 degrees C. It can be considered at more remarkable low temperature, for example, the temperature of less than 60 degrees C, that compressive stress is substantially held with a strength property at infinity.

[0030] It is a point characteristic of the glass manufactured by this new approach that there are few amounts of extraction of alkali metal besides bending strength, i.e., chemical resistance is high. At the purpose which shows this property concretely, it is KNO_3 to the glass of the example 3 of Table 1. In performing chemical-strengthening processing in a bath, the strengthening processing time and temperature were changed again, and the amount of extraction of alkali metal was measured about that each. A result is shown in Table 5 and 6 (when changing ion-exchange temperature). (when changing ion-exchange time amount) It leached by three samples about each case, and the amount of extraction was measured. The result shown in a table was reproducible.

[0031]

[Table 5]

表 1 の実施例 3 の組成を有するガラスについての、一定の塩浴温度 (450°C) での、強化処理時間の関数としての、ハードディスク基板 1 枚あたりのアルカリ金属浸出量 (μg)

強化処理時間 (h)	浸出量 (μg /試料)		
	Na^+	K^+	$\Sigma \text{Na}^+ + \text{K}^+$
0	22	3	25
0.5	2	20	22
1.5	2	22	24
2.0	2	22	24
4.0	2	24	26
10.0	3	16	19
15.0	6	8	14

The strengthening processing time has shown non-tempered glass of 0 hour to the 1st line of Table 5 as an example of a comparison. Distribution of the ion which exuded has fluctuation because a difference is in element distribution in the front face of tempered glass and non-tempered glass. But it is important that the total amount of extraction of the alkali-metal ion of tempered glass is low to the same extent as the case of the glass which has not performed chemical-strengthening processing, while it is surprising. That is, in spite of having performed strengthening processing, good chemical resistance is held. further — being surprised — even if it extends the strengthening processing time, when the amount of extraction of alkali metal hardly increases but ion-exchange time amount, not to mention it, becomes long, it is that the amount of extraction of alkali metal decreases.

[0032]

[Table 6]

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表1の実施例3の組成を有するガラスについての、 一定の強化処理時間（2時間）での、強化処理温度 の関数としての、ハードディスク基板1枚あたりの アルカリ金属の浸出量（ μg ）			
強化処理 温度（ $^{\circ}\text{C}$ ）	浸出量（ $\mu\text{g}/\text{試料}$ ）		
	Na^{+}	K^{+}	$\Sigma\text{Na}^{+} + \text{K}^{+}$
350	6	22	28
400	2	21	23
450	2	22	24
500	3	20	23
550	3	21	24

As shown in Table 6, the amount of extraction of alkali metal is hardly influenced with strengthening processing temperature. [0033] The glass which has the presentation as written and performed chemical-strengthening processing the condition as written shows in Table 7 that it is possible to carry out considerable extent reduction of the thickness, for example by polish, without changing intentionally the amount of alkali-metal extraction, i.e., chemical resistance. This table shows the amount of alkali-metal extraction from the hard disk substrate which has the presentation of the example 3 of Table 1 about the two different hardening processing times. Neither of the cases is before strengthening processing, and this hard disk substrate grinds both sides with cerium oxide until thickness decreases by 10 micrometers after strengthening processing. Residual roughness could be less than 1nm. The thickness of the compressive-stress band before polish was 33 micrometers (strengthening processing time, 2.5 hours) or 40 micrometers (strengthening processing time, 3.0 hours). The value of front Naka was checked by three measurement.

[Table 7]

表1の実施例3の組成を有するハードディスク基板 に、強化処理温度460 $^{\circ}\text{C}$ で、2種の強化処理時間で 強化処理を施し、その後、各事例とも、両面を研磨 して厚さを10 μm 減少させた場合の、ハードディス ク基板1枚あたりのアルカリ金属の浸出量（ μg ）			
強化 処理時間 （h）	浸出量（ $\mu\text{g}/\text{試料}$ ）		
	Na^{+}	K^{+}	$\Sigma\text{Na}^{+} + \text{K}^{+}$
2.5	5	10	15
3.0	5	13	18

The advantage which the method of grinding after performing the approach of the specific embodiment of this invention indicated here, i.e., strengthening processing, from this result has is known clearly. Good chemical resistance is held and the surface quality which might be spoiled by the ion exchange is everlastingly improved by the polish after processing.

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TECHNICAL FIELD

[Field of the Invention] Fracture strength of this invention is high and it is related with the manufacture approach of the glass by which chemical-strengthening processing (chemical reserve stress grant processing) was carried out excellent also in chemical resistance, and use of such glass.

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EFFECT OF THE INVENTION

[Effect of the Invention] The advantage of the new approach of this invention is as follows. That is, the tempered glass manufactured by the approach of this invention has the following properties, and this is a combination peculiar to this invention.

- High bending strength, - A deep compressive-stress band, - That the generated compressive stress does not ease substantially.
- Good surface quality and - High chemical resistance.

Since the tempered glass manufactured by the new approach of this invention has the peculiar property, it is the the best for using it as substrate glass for hard disks. Probably, other effectiveness and advantages of this invention will be clear from the above mentioned explanation and the following examples.

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 TECHNICAL PROBLEM

[Description of the Prior Art] Since glass is divided and has the property of low surface roughness and smooth nature which should be mentioned especially as compared with a metal like aluminum or various metal alloys, when using it as a substrate of a data-hold medium (hard disk), it is advantageous. Such glass for substrates needs to bear the heavy load added chemically, thermally, and mechanically at the time of the inside of manufacture of a hard disk, or use. That is, such glass is heated by the elevated temperature between coatings (for example, based on cathode sputtering), and is cooled after that for a short time. the big mechanical load also at the time of the use as a hard disk — starting — such a load — for example, rotational speed — 3,500 – 10,000rpm and the bolting stress to a revolving shaft — 300N/mm2 **** — it becomes.

[0003] The glass which has not performed strengthening processing will be fractured very easily, if a tensile stress is added. Especially, in the case of thin glass with a thickness of 0.25–3.00mm, a load which was mentioned above only when strengthening processing (reserve stress grant processing) was carried out can be borne. Compared with the glass which has not performed strengthening processing, a load with it is added, and the glass which has performed strengthening processing becomes comparable [the probability of fracture] for the first time. [the low namely, probability fractured also by the predetermined load and] [bigger]

[0004] Since 3mm or more in thickness is needed also at the lowest in order to increase a mechanical strength by heat strengthening (thermal reserve stress grant), the chemical strengthening by the ion exchange in the inside of a salt bath serves as alternative here. In the chemical strengthening of a under from a glass transition point T_g , alkali-metal ion with the small ion diameter in glass is permuted by alkali-metal ion with the big ion diameter in a salt bath, for example, it is Li^+ . Na^+ Na^+ K^+ It permutes. about [consequently, / of the ion-exchange depth] — a compressive-stress band with a thickness [equivalent to two thirds] of about 14–230 micrometers forms — having — 350–900N/mm2 Bending strength is attained.

[0005] One important factor which will be accepted when generating a compressive-stress layer well is the presentation of glass. If Li ion exists in glass, it will become difficult to advance an ion-exchange process. The ion exchange [this / Li^+] of two types, i.e., it is, Na^+ The permutation to depend and Na^+ K^+ It is because the permutation to depend will arise and it is usually necessary to observe the specific mixing ratio of Na salt and K salt, and a narrow temperature requirement in process of the ion exchange. With oxygen ion, the fluoride in glass forms the anion network structure of glass, and can also diffuse big ion easily in such network structure. This will promote reduction of stress. When substrate glass contains comparatively a lot of fluorides, a chemical strengthening is usually the process of whether only a short period of time is attained and coating, for example, either of whether it will be almost lost at the time of heating. The quality of glass concerning the number and size of a defect of solid inclusion, a bubble, etc. at the above mentioned application is also important. This is because a concave hole will arise at the time of polish and the irregularity which cannot be permitted on a front face will arise, if air bubbles are shown in a substrate front face.

[0006] German patent application public presentation official report DE 42 06 268 The lithium content aluminosilicate glass for hard disk substrate glass is indicated by aluminum number. LiO_2 Although ***** is improved by existing, a chemical strengthening also becomes difficult for coincidence. In addition to surface smooth nature with a glass substrate, chemical resistance is also very important for the functionality of a fixed disk. In order to locate reading / writing head of a computer in the point-blank range of about 50nm and to function convenient from the hard disk which is carrying out high-speed rotation, this distance needs to be held correctly. However, resistance does not have the substrate front face of a hard disk to an operation of atmospheric air, and if a front face is ruined (for example, efflorescence), or, adhesive strength with each class by which a front face is ****(ed) on a front face for an operation of atmospheric air is lost and exfoliation arises by the attack of a chemical before a coating activity, the distance of a head and a disk will decrease.

[0007] It is also a problem that the resistance on the front face of glass to water, caustic alkali liquid, or an acid usually decreases by chemical-strengthening processing, i.e., increase of the concentration of comparatively big alkali-metal ion. Not only chemical resistance falls, but [when alkali-metal concentration rises] this is for the attack operation by the chemical to increase, so that alkali-metal ion is large.

[0008] The purpose of this invention is to offer the manufacture approach of the chemically strengthened glass which is excellent also in chemical resistance and bending strength is not only high, but can be especially used suitably as a substrate for hard disks.

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MEANS

[Means for Solving the Problem] In order to attain said purpose, according to this invention, the presentation SiO₂ of the following [oxide criteria] 63.0-67.5-mol %, aluminum 2O₃ 9.5-12.0-mol % and Na₂O 8.5-15.5-mol % and K₂O 2.5-4.0-mol %, MgO 3.0-9.0-mol %, sigma CaO+SrO+BaO+ZnO 0-2.5-mol %, TiO₂ 0.5-1.5-mol %, CeO₂ 0.02-0.5-mol %, As₂O₃ 0-0.35-mol %, SnO₂ 0-1.0-mol % and F₂ 0.05-2.6-mol % — however — SiO₂/aluminum₂O₃ 5.3-6.85 Na₂O/K₂O 3.0-5.6 K₂O [aluminum₂O₃/] 2.8-3.6 aluminum₂O₃/(TiO₂+CeO₂) In the ion-exchange bath which contains more potassium salt than 90 % of the weight in the glass which has 7.6-18.5 The manufacture approach of chemically strengthened glass of reaching in the high fracture strength characterized by performing chemical-strengthening processing over 0.5 - 20-hour immersion time amount at the temperature of 350-550 degrees C, and having high chemical resistance is offered.

[0010]

[Embodiment of the Invention] The requirements for making the compressive-stress band which has a desired property generate at a strengthening (reserve stress grant) process are the presentations of glass. With the aluminosilicate glass used by this invention, it is SiO₂. It is because the melting point will rise superfluously if a content must not exceed 67.5-mol % and this exceeds this content. On the other hand, it is SiO₂. Even if a content becomes less than [63.0 mol %], it does not become, but this is because chemical resistance is spoiled remarkably under in this content. aluminum 2O₃ since it is the same A content must not exceed 12.0-mol %, either and must not be less than [9.5 mol %], either. It is SiO₂ in order to secure the both sides of good acid resistance and good ion-exchange nature. aluminum 2O₃ It is necessary to exist by the ratio which was able to take balance mutually. Namely, SiO₂ / aluminum 2O₃ There must be a mole ratio within the limits of 5.3-6.85.

[0011] There is an alkali-metal oxide as a fundamental component of glass. By combining effectively the clarifier mentioned later according to this invention, it becomes possible to except Li₂O completely, and it becomes possible to attain a desired property to coincidence about the both sides of surface quality and a chemical strengthening with single glass. There must be a Na₂O content in 8.5-15.5-mol % of within the limits. By chemical resistance falling, if a Na₂O content exceeds 15.5-mol %, if lower on the other hand than 8.5-mol %, it will be hard coming to fuse glass in the first place first, and it is Na⁺/K⁺ to the second. The increment in the reinforcement only by the ion exchange will be restricted.

[0012] The component which has an exceptional and surprising operation is K₂O, and this component needs to exist in % of the amount of 2.5-4.0 mols. This component increases the melting nature of glass and promotes the ion-exchange process by K ion in a salt bath of Na ion in glass. Furthermore, a homogenization process is also simplified and it also becomes approaching the condition of request that a bubble is absent. This is for simplifying ****, without spoiling the chemical resistance and chemical-strengthening nature (chemical reserve stress grant nature) which the direction of K₂O increased the basicity of glass, consequently were excellent compared with Na₂O of the number of the said mols. It is only the case of above-mentioned within the limits that same chemical and the glass which has a mechanical property and was excellent in the cellular property can be manufactured easily. Less than [2.5 mol %], when the ratio of aluminum₂O₃ / K₂O is less than 2.8, the content of K₂O The consistency of air bubbles and the size of air bubbles increase, and on the other hand, the content of K₂O is larger than 4.0-mol %, and when the ratio of aluminum₂O₃ / K₂O is larger than 3.6, reinforcement of glass cannot be enough increased between chemical-strengthening processings (chemical reserve stress grant processing). Two sorts of alkali-metal oxides also need to exist by the ratio which was able to take balance mutually. That is, there must be a mole ratio of Na₂O/K₂O within the limits of 3.0-5.6.

[0013] other indispensable components — MgO — it is — the minimum — 3.0-mol % — it is necessary to exist Consequently, the basicity of glass rises and homogenization is promoted. However, under existence of bivalence ion, since Na ion joins together more strongly in aluminosilicate glass structure, MgO is also checking an ion-exchange process. For this reason, MgO must not exceed 9.0-mol % at the maximum. Other alkaline-earth-metal oxides and ZnO also have the same operation. therefore, this glass — CaO, SrO, BaO, and ZnO — total amount sigma CaO+SrO+BaO+ZnO — it is — 0-2.5-mol % — it can contain 0.1 to 2.5% preferably. The thing with MgO more desirable than other alkaline-earth-metal oxides and ZnO is because there are few degrees which spoil chemical resistance than these oxides, while MgO raises melting nature like BaO and CaO. Furthermore, it is TiO₂. It is the indispensable component of glass. TiO₂ 1.5-mol % of that whose content needs to be more than 0.5 mol % — it must not exceed — this — this — it is because trouble arises between melting of a batch that it is out of range.

[0014] In order to obtain the best result about a bubble property, other components, i.e., clarifier, and founding assistants also need to exist in the combination which was able to take balance. Glass is CeO₂ of % of the amount of 0.02-0.5 mols. It is necessary to contain. CeO₂ It not only has a founding function, but it gives the absorbing power of ultraviolet rays with many medicine top problems high enough to glass. Therefore, use of the glass in lighting industry also becomes possible. The initial complement of a clarifier is aluminum 2O₃ which exists in glass. Being influenced by the amount was found out. aluminum 2O₃ which exists in glass The initial complement of a clarifier increases, so that there are many amounts. It is necessary to make it the mole ratio of aluminum₂O₃/(CeO₂+TiO₂) specifically become within the limits of 7.6-18.5. As other clarifiers, it is As₂O₃ not more than 0.35 mol %. And SnO₂ not more than 1.0 mol % It is suitable. It is desirable that at least one side recognizes amount existence beyond 0.02 mol % among two sorts of these components. The glass used in the semantics [there are few bubbles and] that size is small especially in order to be quality is As₂O₃ of % of the amount of 0.02-0.35 mols. It is necessary to contain.

[0015] Glass is F₂ of % of the amount of 0.05-2.6 mols further. It is necessary to contain. The minimum of this range is set up on the need for cellular quality, and an upper limit is set up in view of the above-mentioned operation of the fluoride to the network structure of glass. In the case of arsenic content glass, it is F₂ [0.05-0.7 mol %]. F₂ which is 0.5-2.6-mol % when a content is

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desirable and is arsenic non-containing glass A content is desirable.

[0016] It is possible to create simply the compressive-stress band of high depth which compressive stress maintains over a long period of time according to a chemical strengthening with such glass to a surprising thing, without spoiling the good chemical resistance. 100 % of the weight - 90% of the weight or more of potassium salt is contained, and glass goods are immersed in a salt bath [as / whenever / bath temperature / whose / is 350-550 degrees C] over 0.5 - 20 hours. By such processing, a compressive-stress band about 14 to 230 micrometers or more generates [thickness]. The immersion time amount of long duration is needed, so that temperature is low in that case. All things the anion is stable in the above-mentioned temperature requirement can be used for a salt bath by general potassium salt. A potassium content reduces a salt bath (it usually starts from 100% of potassium salt) for the ion exchange, and when the desired ion-exchange depth is no longer obtained, they are exchanged. It is usually a time of potassium salt becoming 90 % of the weight to become such a situation. It is also possible to use 10 or less % of the weight of other salts, and to lower the melting point of a bath from the beginning. It means that the ion-exchange capacity of a bath exhausts this the part earliness, of course.

[0017] When the ion exchange performs a chemical strengthening on glass, a result whose front face is ruined depending on the case may be brought. In the advantageous embodiment of the new approach of this invention, glass is ground after strengthening. The compressive-stress layer from which it is obtained by this invention that such a series of down stream processing from which the conventional technique differs can be performed is because it is thick, without spoiling the fracture strength excellent in this invention. Although it is desirable to carry out to 25 micrometers or more in thickness and it performs the ion exchange over about 1 hour for that purpose at the temperature of 450 degrees C, as shown in Table 2, even if other processing times and temperature are used for a compressive-stress layer, it is possible for considering as such thickness. If it grinds after strengthening, the glass which has the surface characteristic which could remove again mechanical change produced on the front face, and was excellent between chemical-strengthening processings can be obtained, and, moreover, good chemical resistance will also be maintained. If the approach of this invention is used, since a surface characteristic not only improves, but a **** process can be reduced, the manufacture approach will also be simplified. Polish of glass is performed using cerium oxide and it is made for granularity to be set to less than 1nm with an RMS value (mean square value).

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EXAMPLE

[Example] Table 1 shows some examples of the tempered glass manufactured by the new approach of this invention, and is those presentations and KNO₃. The ion-exchange conditions of a under [a bath], chemical resistance, and many properties relevant to strength are shown.

[0020] Glass was manufactured from the usual raw material in the platinum crucible containing 4l. The raw material was supplied over 8 hours with the melting temperature of 1,580 degrees C. After holding glass to this temperature over 14 hours after that, it cooled to 1,400 degrees C over 8 hours, stirring, and it was poured out in the mold of the graphite which carried out remaining heat to 500 degrees C. In order to conduct a preliminary visual inspection, this casting block was processed into tubing which ground the front face. The glass board to which the circular glass board which has the configuration and dimension of a hard disk substrate, i.e., an outer diameter, was [the hole with a diameter of 20.0mm] thick in 65.0mm by the usual approach, and it was thick in the center in 0.635mm from this casting block was manufactured. It is KNO₃ to grinding and this ground glass board in a precision. Chemical-strengthening processing was performed under the monograph affair shown in the table in the bath.

[0021] Each property and parameter which were shown all over Table 1 are measured using the following physical analysis. Bending strength is measured by the approach of the following usually used in glass industry, and aims at the load produced in actual use. What was performed is the so-called duplex ring trial, and in this trial, a diameter lays it on the metal support ring which has the annular cutter of hardening steel with a diameter somewhat smaller than 60mm ($\phi = 65\text{mm}$), i.e., the test objective glass board, in the chemical-strengthening processing glass board which has the configuration and dimension of a hard disk substrate, and it doubles a core. On this glass board, another metal support ring which has a steel cutter is laid similarly, and a core is doubled. A diameter is 25mm and this cutter has a diameter somewhat larger a little than the hole ($\phi = 20\text{mm}$) of the center of a hard disk substrate. Push, therefore a hard disk substrate will be joined the rate for 2mm/by the force which continues increasing with constant speed in the glass board by which the cutter of the ring by the side of besides was laid on the cutter of a lower ring. Let the load in the time of a substrate fracturing be bending strength (N/mm²). In this trial, a load regards it as success, when fracture arises for the first time exceeding 100 Ns.

[0022] Compressive stress is measured by the stress-optical method. That is, when compressive stress has joined the glass plate, change arises in the refractive index of an parallel and perpendicular direction to the stress direction, and a glass plate comes to show a birefringence. The birefringence, i.e., the difference of these refractive indexes, is proportional to the added stress according to the stress-optical multiplier of the glass concerned, and it is measured from the optical path difference after the reflection in respect of the glass of a perpendicular and parallel polarization light.

[0023] The thickness of a compressive-stress band is the following, and is made and measured. A glass sample is observed on the wavelength of 546nm by the bottom of a polarization microscope. From the reasons of a balance, compressive stress has joined all front faces and, as for the sample to which the ion exchange was given, the tensile stress has joined the interior. In order to measure stress, a sample is placed between two polarizers made to cross. The stress which has joined the sample produces brightness in stress double refraction, therefore the optical path of a microscope. The transition (zero-order neutral band) to compressive stress from a tensile stress is visible clearly as a dark-colored broadcloth band under a microscope. The distance from a sample edge to a zero-order band serves as measured value of the thickness of a compressive-stress band. Since the above-mentioned glass board was too thin for performing this measurement, it used the piece of glass which was manufactured and hardened on the same conditions as this glass board and whose thickness is 2mm in 6mmx50mm for this measurement.

[0024] Knoop hardness is measured according to DIN52333. The quick and simple test method which used easy equipment is indispensable to chemical-resistant measurement. There is no standard test method which specialized in the glass data-hold medium despite today. Although various kinds of test methods which investigate the chemical resistance of glassware are known for glass industry, those approaches are unsuitable although the chemical resistance of a hard disk substrate is judged by various reasons.

[0025] The so-called amount of alkali extraction of the disk manufactured by the new approach of this invention can be carried out simple, and is judged by the new approach to obtain a very significant result. Here, vocabulary called the amount of alkali extraction shall mean the total amount of the alkali-metal ion eluted from a sample in the following trial carried out on condition that the following. The glass disk [finishing / strengthening processing] which has an above-mentioned configuration and an above-mentioned dimension, i.e., an outer diameter, is 65.0mm, a sample is the glass board with a thickness of 0.635mm to which the hole with a diameter of 20.00mm opened in the center, an edge picks grinding and a field to a precision, and a front face is ground until it serves as less than 1nm of RMS roughness using cerium oxide. With the condition of having washed and having become wet with the last washing process over 1 / 4 hours at the room temperature in the ultrasonic bath using deionized water, the sample which performed strengthening processing, or the sample which performed strengthening processing and polish in the suitable embodiment was immersed into 25ml of 80-degree C deionized water, and was left as it was for 24 hours. The amount of the alkali-metal ion which exuded was measured by atomic absorption analysis. The amount (mg) of the alkali metal which exuded in each example is a thing about one sample respectively.

[0026]

[Table 1]

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本発明の新規な方法によって製造した強化ガラスの組成 (モル%、酸化物基準) 及びその本質的特性							
実施例No.	1	2	3	4	5	6	7
SiO ₂	65.54	67.32	63.60	63.67	66.26	66.89	67.36
Al ₂ O ₃	9.60	11.18	11.91	9.74	10.91	10.91	11.28
Na ₂ O	8.66	13.58	12.49	16.02	11.30	11.30	12.82
K ₂ O	2.68	3.17	3.48	2.89	3.82	3.82	3.82
MgO	8.62	3.29	6.51	3.97	3.25	3.25	3.25
CaO + SrO + BaO + ZnO	1.25	0.24	0.47	0.14	0.12	0.12	0.24
SnO ₂	1.0	—	—	0.15	—	—	0.15
TiO ₂	1.19	0.54	0.66	0.64	1.23	0.66	0.54
CeO ₂	0.06	0.46	0.02	0.15	0.19	0.19	0.15
F ₂	1.41	0.09	0.51	2.53	2.59	2.59	0.22
As ₂ O ₃	—	0.17	0.35	0.05	0.33	0.33	0.17
イ ¹ 交換温度 (°C)	500	450	400	450	480	480	520
イ ¹ 交換時間 (時間)	10	1.5	5	4	6	6	20
圧縮応力帯域の厚さ (μm)	105	35	45	52	128	125	220
アルカリ金属の浸出量 (μg)	21	20	24	22	18	23	17
300 °Cでの「応力緩和」 (h)	950	>1000	>1000	700	800	850	>1000
曲げ強さ (N/mm ²)	720	490	410	560	640	620	900
メ-フ 硬度 (KH)	585	590	600	545	562	568	609
弾性率E (kN/mm ²)	70	71	72	66	68	68	72
熱膨張係数 α _{20/300} (10 ⁻⁶ /K)	8.2	8.9	9.1	9.6	9.1	9.1	8.9
ガラス 遷移温度T _g	595	632	618	565	573	579	626

The amount of extraction of alkali metal means the total amount of extraction of the alkali-metal ion per hard disk substrate at the time of performing an above-mentioned trial under above-mentioned conditions (μg). Rhine of "stress relaxation (h)" shows the time amount (h) taken to decrease until the thickness of a compressive-stress band becomes measurable, when it is made into constant temperature (300 degrees C). Incidentally, change of the thickness which exceeds 4 micrometers is measurable. It is as having already explained the used optical means. Such reduction of the thickness of a compressive-stress band is easier to measure than compressive-stress relaxation itself in relation to reduction of compressive stress.

[0027] KNO₃ In the bath, while carrying out chemistry hardening of the glass which has the presentation of the example 3 of Table 1, ion-exchange time amount was changed from 1 / 2 hours to 15 hours, and whenever [bath temperature] was changed from 350 degrees C to 550 degrees C. The thickness (micrometer) of the obtained compressive-stress band is shown in Table 2. The range of the thickness of a compressive-stress band was 14-230 micrometers, and the point which needs such long immersion time amount that temperature is low was as prediction.

[Table 2]

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表 1 の実施例 3 の組成を有するガラスについての、イオン交換時間又は塩浴温度の関数としての圧縮応力帯域 (μm)

イオン交換時間 (h)	浴温度 ($^{\circ}\text{C}$)				
	350	400	450	500	550
0.5		14	20	38	46
1			26	55	68
1.5		20	30	60	90
2.5		31			
4			42		121
5		45		98	
8			75		
10		63	90	132	182
15	47	72	103	165	230

[0028] Thus, it depends for the thickness of a compressive-stress band to ion-exchange time amount (when ion-exchange temperature is fixed) and the both sides of ion-exchange temperature (when ion-exchange time amount is fixed) clearly. Table 3 shows that it is certainly applied about bending strength, although such a dependency is not applied to the compressive stress in a front face as it is. What was chosen as operation glass also in this case was glass which has the presentation of the example 3 of Table 1.

[Table 3]

表 1 の実施例 3 の組成を有するガラス についての、一定の塩浴温度 (450 $^{\circ}\text{C}$) でのイオン交換時間の関数としての圧縮応力帯域の厚さ、表面での圧縮応力、及び曲げ強さ			
イオン交換時間 (h)	圧縮応力帯域 の厚さ (μm)	表面での圧縮 応力 (N/mm^2)	曲げ強さ (N/mm^2)
1.5	30	880 ± 30	430
15	103	775 ± 30	800

Since it has the value of the above very good bending strength, the tempered glass manufactured by the new approach of this invention is the optimal when bearing the mechanical load by which the current load is carried out to the hard disk (high speed of a future hard disk), or a load will be carried out to it.

[0029] The temperature dependence of the stress relaxation which made reference in relation to the above-mentioned table 1 is shown in Table 4. It is the hard disk substrate manufactured for this purpose from the glass which has the presentation of the example 7 of Table 1 KNO3 It was made to harden over 20 hours in a bath at 520 degrees C. Compressive stress is 2 800Ns/mm. The compressive-stress band which is 220 micrometers was formed. Table 4 is each temperature and shows the time amount which passed by the time reduction of the thickness of a compressive-stress band was observed.

[Table 4]

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表 1 の実施例 7 の組成を有するガラスについての、所定温度で圧縮応力帯域の厚さに測定可能な減少 ($4\mu\text{m}$) が生じるまで経過した時間

温度 ($^{\circ}\text{C}$)	時間 (h)
300	> 1000
350	500
400	100
500	30

If it extrapolates, by the time stress relaxation arises, 50,000 hours or more will pass at the temperature of 200 degrees C. It can be considered at more remarkable low temperature, for example, the temperature of less than 60 degrees C, that compressive stress is substantially held with a strength property at infinity.

[0030] It is a point characteristic of the glass manufactured by this new approach that there are few amounts of extraction of alkali metal besides bending strength, i.e., chemical resistance is high. At the purpose which shows this property concretely, it is KNO_3 to the glass of the example 3 of Table 1. In performing chemical-strengthening processing in a bath, the strengthening processing time and temperature were changed again, and the amount of extraction of alkali metal was measured about that each. A result is shown in Table 5 and 6 (when changing ion-exchange temperature). (when changing ion-exchange time amount) It leached by three samples about each case, and the amount of extraction was measured. The result shown in a table was reproducible.

[0031]

[Table 5]

表 1 の実施例 3 の組成を有するガラスについての、一定の塩浴温度 (450°C) での、強化処理時間の関数としての、ハードディスク基板 1 枚あたりのアルカリ金属浸出量 (μg)

強化処理時間 (h)	浸出量 ($\mu\text{g}/\text{試料}$)		
	Na^+	K^+	$\Sigma \text{Na}^+ + \text{K}^+$
0	22	3	25
0.5	2	20	22
1.5	2	22	24
2.0	2	22	24
4.0	2	24	26
10.0	3	16	19
15.0	6	8	14

The strengthening processing time has shown non-tempered glass of 0 hour to the 1st line of Table 5 as an example of a comparison. Distribution of the ion which exuded has fluctuation because a difference is in element distribution in the front face of tempered glass and non-tempered glass. But it is important that the total amount of extraction of the alkali-metal ion of tempered glass is low to the same extent as the case of the glass which has not performed chemical-strengthening processing, while it is surprising. That is, in spite of having performed strengthening processing, good chemical resistance is held. further — being surprised — even if it extends the strengthening processing time, when the amount of extraction of alkali metal hardly increases but ion-exchange time amount, not to mention it, becomes long, it is that the amount of extraction of alkali metal decreases.

[0032]

[Table 6]

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表1の実施例3の組成を有するガラスについての、一定の強化処理時間（2時間）での、強化処理温度の関数としての、ハードディスク基板1枚あたりのアルカリ金属の浸出量（ μg ）

強化処理 温度（ $^{\circ}\text{C}$ ）	浸出量（ $\mu\text{g}/\text{試料}$ ）		
	Na^{+}	K^{+}	$\Sigma\text{Na}^{+} + \text{K}^{+}$
350	6	22	28
400	2	21	23
450	2	22	24
500	3	20	23
550	3	21	24

As shown in Table 6, the amount of extraction of alkali metal is hardly influenced with strengthening processing temperature. [0033] The glass which has the presentation as written and performed chemical-strengthening processing the condition as written shows in Table 7 that it is possible to carry out considerable extent reduction of the thickness, for example by polish, without changing intentionally the amount of alkali-metal extraction, i.e., chemical resistance. This table shows the amount of alkali-metal extraction from the hard disk substrate which has the presentation of the example 3 of Table 1 about the two different hardening processing times. Neither of the cases is before strengthening processing, and this hard disk substrate grinds both sides with cerium oxide until thickness decreases by 10 micrometers after strengthening processing. Residual roughness could be less than 1nm. The thickness of the compressive-stress band before polish was 33 micrometers (strengthening processing time, 2.5 hours) or 40 micrometers (strengthening processing time, 3.0 hours). The value of front Naka was checked by three measurement.

[Table 7]

表1の実施例3の組成を有するハードディスク基板に、強化処理温度460 $^{\circ}\text{C}$ で、2種の強化処理時間で強化処理を施し、その後、各事例とも、両面を研磨して厚さを10 μm 減少させた場合の、ハードディスク基板1枚あたりのアルカリ金属の浸出量（ μg ）

強化 処理時間 （h）	浸出量（ $\mu\text{g}/\text{試料}$ ）		
	Na^{+}	K^{+}	$\Sigma\text{Na}^{+} + \text{K}^{+}$
2.5	5	10	15
3.0	5	13	18

The advantage which the method of grinding after performing the approach of the specific embodiment of this invention indicated here, i.e., strengthening processing, from this result has is known clearly. Good chemical resistance is held and the surface quality which might be spoiled by the ion exchange is everlastingly improved by the polish after processing.

[Translation done.]

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(54) 【発明の名称】 化学強化処理されたガラスの製造方法及びその使用

(57) 【要約】

【課題】 曲げ強さや耐薬品性など非常に高い表面品質を有し、特にハードディスク用基板として好適に使用できる化学強化処理されたガラスの製造方法を提供する。

【解決手段】 TiO_2 、 CeO_2 、及び F_2 を含む SiO_2 - Al_2O_3 - M_2O - MO 系の Li 、 O 非含有のガラスを、カリウム塩浴中で化学的イオン交換処理に付す。好適な態様においては、化学強化処理後、研磨を施す。

【特許請求の範囲】

【請求項1】 酸化物基準で以下の組成

SiO₂ 63.0～67.5モル%、
 Al₂O₃ 9.5～12.0モル%、
 Na₂O 8.5～15.5モル%、
 K₂O 2.5～4.0モル%、
 MgO 3.0～9.0モル%、
 Σ CaO+SrO+BaO+ZnO 0～2.5*

SiO₂/Al₂O₃Na₂O/K₂OAl₂O₃/K₂OAl₂O₃/(TiO₂+CeO₂)

を有するガラスに、90重量%より多いカリウム塩を含むイオン交換浴中で、350～550℃の温度にて、0.5～20時間の浸漬時間にわたって化学強化処理を施すことを特徴とする高い破断強さ及び高い耐薬品性を有する化学強化処理されたガラスの製造方法。

【請求項2】 使用するガラスがAs₂O₃及びSnO₂よりなる群から選ばれる少なくとも1種の成分を、少なくとも0.02モル%含有することを特徴とする請求項1に記載の方法。

【請求項3】 使用するガラスが、0.02～0.35モル%のAs₂O₃を含有することを特徴とする請求項1又は2に記載の方法。

【請求項4】 化学強化処理の後に、ガラスを研磨することを特徴とする請求項1乃至3のいずれか一項に記載の方法。

【請求項5】 請求項1乃至4のいずれか一項に記載の方法に従って製造したガラスの、ハードディスク用ガラス基板としての使用。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、破断強さが高く、耐薬品性にも優れた化学強化処理（化学的予備応力付与処理）されたガラスの製造方法及びそのようなガラスの使用に関する。

【0002】

【従来の技術と発明が解決しようとする課題】ガラスは、アルミニウムや各種金属合金のような金属と比較して、とりわけ、低い表面粗さと平滑性という特筆すべき特性を有していることから、データ保持媒体（ハードディスク）の基板として使用するうえで有利である。こうした基板用ガラスは、ハードディスクの製造中や使用時に、化学的、熱的、及び機械的に加えられる高負荷に耐える必要がある。すなわち、こうしたガラスは、コーティング（例えば、カソードスパッタリングによる）の間に高温に熱せられ、その後短時間に冷却される。ハードディスクとしての使用時にも大きな機械的負荷がかかり、そうした負荷は、例えば回転速度で3,500～10,000rpm、回転軸への締め付け応力で300N

*モル%、

TiO₂ 0.5～1.5モル%、CeO₂ 0.02～0.5モル%、As₂O₃ 0～0.35モル%、SnO₂ 0～1.0モル%、F₂ 0.05～2.6モル%、

但し、

5.3～6.85、

3.0～5.6、

2.8～3.6、

7.6～18.5

/mm²ともなる。

【0003】強化処理を施していないガラスは、引っ張り応力が加わると極めて容易に破断してしまう。特に、厚さ0.25～3.00mmの薄いガラスの場合、強化処理（予備応力付与処理）がされた場合にのみ上述したような負荷に耐えることができる。強化処理を施していないガラスに比べて、強化処理を施してあるガラスは、所定の荷重でも破断する確率が低く、すなわち、より大きな荷重が加えられて、破断の確率がはじめて同程度となる。

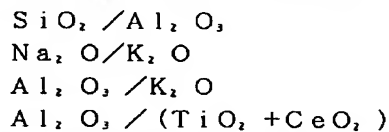
【0004】熱強化（熱的予備応力付与）によって機械的強度を増大させるには、最低でも厚さ3mm以上が必要とされるので、塩浴中でのイオン交換による化学強化がここでの選択肢となる。ガラス転移点T_gより下での化学強化においては、ガラス中のイオン直径の小さなアルカリ金属イオンが、塩浴中のイオン直径の大きなアルカリ金属イオンによって置換され、例えば、Li⁺がNa⁺によって、Na⁺がK⁺によって置換される。その結果、イオン交換深さの約2/3に相当する厚さ約14～230μmの圧縮応力帯域が形成され、350～900N/mm²の曲げ強さが達成される。

【0005】圧縮応力層をうまく生成するうえでのもう一つの重要な要因は、ガラスの組成である。ガラス中にLiイオンが存在すると、イオン交換過程を進めることが困難となる。これは、2つのタイプのイオン交換、すなわち、Li⁺のNa⁺による置換と、Na⁺のK⁺による置換とが生じることとなり、また、イオン交換の過程では、通常、Na塩とK塩の特定の混合比、及び狭い温度範囲を遵守する必要があるからである。ガラス中のフッ化物は、酸素イオンとともに、ガラスの陰イオン網状構造を形成しており、こうした網状構造中では、大きなイオンも容易に拡散できる。このことが、応力の低減を促進することになる。基板ガラスが比較的多量のフッ化物を含有している場合には、化学強化は、通常、短期間しか達成されないか、あるいはコーティングの過程、例えば加熱時におおかた失われてしまうかのいずれかである。前記した用途では、固型混在物や泡などの欠陥の数及びサイズに関するガラスの品質も重要である。これ

は、基板表面に気泡があったりすると、研磨時に凹孔が生じ、表面に許容し得ない凹凸が生じてしまうからである。

【0006】ドイツ特許出願公開公報DE 42 06 268 A1号には、ハードディスク基板ガラス用のリチウム含有アルミノケイ酸塩ガラスが記載されている。LiO₂が存在することによって、精澄性が改善されるものの、化学強化も同時に困難となる。ガラス基板では、表面の平滑性に加えて、耐薬品性も、固定ディスクの機能性にとって極めて重要である。コンピュータの読み/書きヘッドは、高速回転しているハードディスクから約50nmという至近距離に位置しており、支障なく機能するためには、この距離が正確に保持される必要がある。しかし、ハードディスクの基板表面が大気的作用に対して耐性がなく、コーティング作業の前に化学物質の攻撃によって表面が（例えば風解によって）荒れてしまったり、大気的作用のために、表面が、表面上に設けられる各層との接着力を喪失して剥離が生じてしまったりすると、ヘッドとディスクとの距離が低減することになってしまう。

【0007】水、苛性アルカリ液、あるいは酸に対するガラス表面の耐性が、通常、化学強化処理、すなわち、比較的大きなアルカリ金属イオンの濃度の増大によって低減してしまうことも問題である。これは、アルカリ金*



を有するガラスに、90重量%より多いカリウム塩を含むイオン交換浴中で、350～550℃の温度にて、0.5～20時間の浸漬時間にわたって化学強化処理を施すことを特徴とする高い破断強さ及び高い耐薬品性を有する化学強化ガラスの製造方法が提供される。

【0010】

【発明の実施の形態】強化（予備応力付与）工程で、所望の特性を有する圧縮応力帯域を生成させるための要件は、ガラスの組成である。本発明で使用するアルミノケイ酸塩ガラスでは、SiO₂含量が67.5モル%を超えてはならず、これは、この含量を超えると、融点が過剰に上昇してしまうからである。一方、SiO₂含量は63.0モル%未満となってもならず、これは、この含量未満では、耐薬品性が著しく損なわれるからである。同じ理由から、Al₂O₃含量も12.0モル%を超えてはならず、9.5モル%未満であってもならない。良好な耐酸性と良好なイオン交換性の双方を確保するためには、SiO₂とAl₂O₃は、互いに均衡のとれた比率で存在する必要がある。すなわち、SiO₂/Al₂O₃のモル比は、5.3～6.85の範囲内になければならない。

【0011】ガラスの基本的成分として、アルカリ金属

* 属濃度が上昇することによって耐薬品性が低下するばかりでなく、アルカリ金属イオンが大きいほど、薬品による攻撃作用が増大するためである。

【0008】本発明の目的は、曲げ強さが高いだけでなく、耐薬品性にも優れ、特にハードディスク用基板として好適に用いることができる化学強化ガラスの製造方法を提供することにある。

【0009】

【課題を解決するための手段】前記目的を達成するために、本発明によれば、酸化物基準で以下の組成

SiO ₂	63.0～67.5モル%
Al ₂ O ₃	9.5～12.0モル%
Na ₂ O	8.5～15.5モル%
K ₂ O	2.5～4.0モル%
MgO	3.0～9.0モル%
Σ CaO+SrO+BaO+ZnO	0～2.5モル%
TiO ₂	0.5～1.5モル%
CeO ₂	0.02～0.5モル%
As ₂ O ₃	0～0.35モル%
SnO ₂	0～1.0モル%
F ₂	0.05～2.6モル%

但し、

5.3～6.85、
3.0～5.6、
2.8～3.6、
7.6～18.5

酸化物がある。後述する清澄剤を本発明に従って効果的に組み合わせることにより、Li₂Oを完全に除外することが可能となり、単一のガラスで表面品質と化学強化の双方について所望の特性を同時に達成することが可能となる。Na₂O含量は、8.5～15.5モル%の範囲内になければならない。Na₂O含量が15.5モル%を超えると、耐薬品性が低下してしまい、一方、8.5モル%より低いと、まず第一に、ガラスが溶融し難くなり、第二に、Na⁺/K⁺のイオン交換のみによる強度の増加が制限されてしまう。

【0012】格別かつ驚くべき作用を有する成分はK₂Oであり、この成分は、2.5～4.0モル%の量で存在する必要がある。この成分は、ガラスの溶融性を増大させ、ガラス中のNaイオンの、塩浴中のKイオンによるイオン交換過程を促進する。さらに、均質化過程も簡素化され、泡の不在という所望の状態に近づくこととなる。これは、同モル数のNa₂Oと比べて、K₂Oの方がガラスの塩基性を増大し、その結果、優れた耐薬品性や化学強化性（化学的予備応力付与性）を損なうことなく、精澄を簡単にするためである。同じ化学的及び機械的特性を有し、気泡特性の優れたガラスを簡単に製造できるのは、上述の範囲内の場合だけである。K₂Oの

含量が2.5モル%未満で、 Al_2O_3/K_2O の比が2.8未満の場合には、気泡の密度及び気泡のサイズが増大し、一方、 K_2O の含量が4.0モル%より大きく、 Al_2O_3/K_2O の比が3.6より大きい場合には、化学強化処理（化学的予備応力付与処理）の間にガラスの強度を充分増大させることができない。2種のアルカリ金属酸化物も、互いに均衡のとれた比率で存在する必要がある。すなわち、 Na_2O/K_2O のモル比は、3.0～5.6の範囲内になければならない。

【0013】他の必須の成分は MgO であり、最低でも3.0モル%存在する必要がある。その結果、ガラスの塩基性度が上昇し、均質化が促進される。しかしながら、二価イオンの存在下では、アルミノケイ酸塩ガラス構造中で Na イオンがより強く結合するので、 MgO はイオン交換過程を阻害することとなる。このため、 MgO は、最大でも9.0モル%を越えてはならない。他のアルカリ土類金属酸化物及び ZnO も、同様の作用を有する。したがって、このガラスは、 CaO 、 SrO 、 BaO 及び ZnO を、総量 $\Sigma CaO + SrO + BaO + ZnO$ で、0～2.5モル%、好ましくは0.1～2.5%含有することができる。 MgO が、他のアルカリ土類金属酸化物及び ZnO より好ましいのは、 MgO が、 BaO 、 CaO と同様に溶解性を向上させる一方で、これらの酸化物より耐薬品性を損なう度合いが少ないからである。さらに TiO_2 もガラスの必須の成分である。 TiO_2 の含量は、0.5モル%以上である必要があるものの、1.5モル%を越えてはならず、これは、この範囲外であると、バッチの溶融の間に支障が生じるからである。

【0014】泡特性に関して最良の結果を得るためには、他の成分、即ち清澄剤及び清澄助剤も、均衡のとれた組み合わせで存在する必要がある。ガラスは0.02～0.5モル%の量の CeO_2 を含有する必要がある。 CeO_2 は、清澄機能を有するばかりでなく、ガラスに、医学上問題の多い紫外線の充分に高い吸収能を付与するものである。したがって、照明産業でのガラスの使用も可能となる。清澄剤の必要量は、ガラス中に存在する Al_2O_3 の量に左右されることが見い出された。ガラス中に存在する Al_2O_3 の量が多いほど、清澄剤の必要量が増大する。具体的には、 $Al_2O_3/(CeO_2 + TiO_2)$ のモル比が、7.6～18.5の範囲内となるようにする必要がある。その他の清澄剤としては、0.35モル%以下の As_2O_3 及び1.0モル%以下の SnO_2 が適当である。これらの2種の成分のうち、少なくとも一方が、0.02モル%以上の量存在するのが好ましい。泡の数が少なく、サイズが小さいという意味で特に高品質とするためには、使用するガラスは、0.02～0.35モル%の量の As_2O_3 を含有する必要がある。

【0015】ガラスは、さらに、0.05～2.6モル

%の量の F 、も含有する必要がある。この範囲の下限は、気泡品質の必要上設定されたものであり、上限は、ガラスの網状構造に対するフッ化物の前述の作用に鑑みて設定されたものである。ヒ素含有ガラスの場合、0.05～0.7モル%の F 、含量が好ましく、ヒ素非含有ガラスの場合、0.5～2.6モル%の F 、含量が好ましい。

【0016】驚くべきことに、こうしたガラスでは、化学強化によって、その良好な耐薬品性を損なうことなく、圧縮応力が長期にわたって持続する高深度の圧縮応力帯域を簡単に作出することが可能である。ガラス物品を、100重量%～90重量%以上のカリウム塩を含有し、浴温度が350～550℃であるような塩浴に、0.5～20時間にわたって浸漬する。こうした処理によって、厚さが約14 μm から230 μm 以上の圧縮応力帯域が生成する。その際、温度が低いほど、長時間の浸漬時間が必要となる。塩浴には、一般的なカリウム塩で、上記の温度範囲でその陰イオンが安定であるようなものは全て使用することができる。塩浴（通常、カリウム塩100%から開始する）は、イオン交換のためにカリウム含量が低減し、所望のイオン交換深さが得られなくなった時点で交換する。こうした状況となるのは、通常、カリウム塩が90重量%となった時点である。最初から、10重量%以下の他の塩を使用して、浴の融点を下げることも可能である。このことは、もちろん、浴のイオン交換能力が、その分早めに消耗することを意味する。

【0017】ガラスに、イオン交換によって化学強化を行うと、場合によっては、表面が荒れてしまう結果となることもある。本発明の新規な方法の有利な実施態様では、強化後にガラスを研磨する。本発明で、優れた破断強さを損なうことなく、従来技術とは異なるこうした一連の処理工程を行うことができるのは、本発明で得られる圧縮応力層が厚いからである。圧縮応力層は、厚さ25 μm 以上とするのが好ましく、そのためには、例えば、イオン交換を、450℃の温度で約1時間にわたって行うが、表2に示すように、他の処理時間及び温度を使用しても、こうした厚さとすることは可能である。強化後に研磨を行うと、化学強化処理の間に表面に生じた機械的変化を再び取り除くことができ、優れた表面特性を有するガラスを得ることができ、しかも、良好な耐薬品性も保たれる。本発明の方法を用いると、表面特性が向上するばかりでなく、精澄工程を減らすこともできるので、製造方法も簡素化されることとなる。ガラスの研磨は、酸化セリウムを用いて行い、粗さがRMS値（二乗平均値）で1nm未満となるようにする。

【0018】

【発明の効果】本発明の新規な方法の利点は、以下のとおりである。すなわち、本発明の方法で製造した強化ガラスは、以下のような特性を兼備しており、これは、本

発明に独特な組み合わせである。

- ・ 高い曲げ強さ、
- ・ 深い圧縮応力帯域、
- ・ 生成した圧縮応力が実質的に緩和することがないこと、
- ・ 良好な表面品質、及び
- ・ 高い耐薬品性。

本発明の新規な方法で製造した強化ガラスは、独特の特性を有しているため、ハードディスク用基板ガラスとして使用するのに最適である。本発明の他の効果及び利点は、前記した説明及び以下の実施例から明らかである。

【0019】

【実施例】表1は、本発明の新規な方法で製造した強化ガラスの幾つかの例を示しており、それらの組成、 KNO_3 、浴中でのイオン交換条件、耐薬品性及び強さに関連した諸特性を示す。

【0020】ガラスは、4リットル入りの白金るつば中で、通常の原材料から製造した。原材料は、1,580℃の熔融温度にて、8時間にわたって投入した。ガラスは、その後14時間にわたってこの温度に保持してから、攪拌しながら8時間かけて1,400℃まで冷却し、500℃に余熱しておいた黒鉛の型内に注いだ。予備的な目視検査を行うために、この铸造ブロックを、表面を研磨した管に加工した。この铸造ブロックから、通常の方法で、ハードディスク基板の形状と寸法を有する円形のガラス盤、すなわち、外径が65.0mm、厚さが0.635mmで、直径20.0mmの孔が中央にあったガラス盤を製造した。精密に研削、研磨したこのガラス盤に、 KNO_3 、浴中で、表に示した各条件下にて、化学強化処理を行った。

【0021】表1中に示した各特性及びパラメータは、以下の物理的分析法を用いて測定したものである。曲げ強さは、ガラス産業で通常使用されている以下の方法で測定し、実際の使用において生ずる負荷を目標とする。行ったのはいわゆる二重環試験で、この試験では、ハードディスク基板の形状と寸法を有する化学強化処理ガラス盤を、直径が60mm、即ち、試験対象ガラス盤($\phi=65\text{mm}$)より直径が多少小さめの焼入鋼製の環状カッターを有する金属製の支持環の上に載置し、中心を合わせる。このガラス盤の上に、鋼製カッターを有する別の金属製支持環を同様に載置し、中心を合わせる。このカッターは、直径が25mmで、ハードディスク基板中央の孔($\phi=20\text{mm}$)より、直径が多少大きめである。この上側の環のカッターが、下側の環のカッター上に載置されたガラス盤を2mm/分の速度で押し、したがって、ハードディスク基板には、一定速度で増大しつづける力が加わることになる。基板が破断した時点での荷重を、曲げ強さ(N/mm^2)とする。この試験では、荷重が100Nを越えてはじめて破断が生じる場合

に、合格とみなす。

【0022】圧縮応力は、応力-光学法によって測定する。すなわち、ガラス板に圧縮応力が加わっている場合には、応力方向に対して平行及び垂直な方向の屈折率に変化が生じ、ガラス板が複屈折を示すようになる。複屈折、すなわち、これらの屈折率の差は、当該ガラスの応力-光学係数に応じて、付加された応力に比例しており、垂直及び平行な偏光光のガラス面での反射後の光路差から測定される。

【0023】圧縮応力帯域の厚さは、以下のようにして測定する。ガラス試料を、偏光顕微鏡下により546nmの波長で観察する。イオン交換を施された試料は、平衡上の理由から、全表面に圧縮応力が加わっており、内部には引っ張り応力が加わっている。応力を測定するために、2つの交差させた偏光子の間に試料を置く。試料に加わっている応力は、応力複屈折ゆえに、顕微鏡の光路に輝きを生じる。引っ張り応力から圧縮応力への遷移(0次のニュートラル帯域)は、顕微鏡下では、ブロードな暗色の帯としてはっきり見える。試料端部から0次帯域までの距離が、圧縮応力帯域の厚さの測定値となる。上述のガラス盤は、この測定を行うには薄すぎるので、この測定には、このガラス盤と同一条件で製造、硬化した、6mm×50mmで、厚さが2mmのガラス片を使用した。

【0024】ヌーブ硬度は、DIN52333に従って測定する。耐薬品性の測定には、簡単な装置を使用した、迅速かつ簡便な試験方法が不可欠である。今日のところ、ガラス製データ保持媒体に特化した標準的な試験方法はない。ガラス産業では、ガラス製品の耐薬品性を調べる各種の試験方法が知られているが、それらの方法は、様々な理由で、ハードディスク基板の耐薬品性を判定するのには不適當である。

【0025】本発明の新規な方法で製造したディスクのいわゆるアルカリ浸出量は、簡便に実施でき、極めて有意な結果の得られる新規な方法によって判定する。ここで、アルカリ浸出量という用語は、下記の条件で実施した下記の試験で試料から溶出するアルカリ金属イオンの総量を意味するものとする。試料は、上述の形状及び寸法を有する強化処理済みのガラス円盤、即ち、外径が65.0mmで、直径20.0mmの孔が中央にあいた、厚さ0.635mmのガラス盤で、端部は精密に研削、面取りし、表面は酸化セリウムを使用してRMS荒さ1nm未満となるまで研磨してある。強化処理を行った試料、あるいは好適な実施態様では強化処理及び研磨を行った試料は、超音波浴中で、脱イオン水を用いて室温で1/4時間にわたる最終洗浄工程で洗浄し、湿った状態のまま、80℃の脱イオン水25mlの中に浸漬し、24時間そのまま放置した。浸出したアルカリ金属イオンの量を、原子吸光分光分析によって測定した。各実施例で浸出したアルカリ金属の量(μg)は、各々1

試料についてのものである。

*【表1】

【0026】

*

本発明の新規な方法によって製造した強化ガラスの組成 (モル％、酸化物基準) 及びその本質的特性							
実施例No.	1	2	3	4	5	6	7
SiO ₂	65.54	67.32	63.60	63.67	66.26	66.83	67.36
Al ₂ O ₃	9.60	11.18	11.91	9.74	10.91	10.91	11.28
Na ₂ O	8.66	13.68	12.49	16.02	11.30	11.30	12.82
K ₂ O	2.68	3.17	3.48	2.89	3.82	3.82	3.82
MgO	8.62	3.29	6.51	3.97	3.25	3.25	3.25
CaO + SrO + BaO + ZnO	1.25	0.24	0.47	0.14	0.12	0.12	0.24
SnO ₂	1.0	—	—	0.15	—	—	0.15
TiO ₂	1.19	0.54	0.66	0.64	1.23	0.66	0.54
CeO ₂	0.06	0.46	0.02	0.15	0.19	0.19	0.15
F ₂	1.41	0.09	0.51	2.53	2.59	2.59	0.22
As ₂ O ₃	—	0.17	0.35	0.05	0.33	0.33	0.17
交換温度 (°C)	500	450	400	450	480	480	520
交換時間 (時間)	10	1.5	5	4	6	6	20
圧縮応力帯域の厚さ (μm)	105	35	45	52	128	125	220
アルカリ金属の浸出量 (μg)	21	20	24	22	18	23	17
300 °Cでの「応力緩和」 (h)	950	>1000	>1000	700	800	850	>1000
曲げ強さ (N/mm ²)	720	490	410	560	640	620	900
モース硬度 (Kf)	585	590	600	545	562	568	609
弾性率E (kN/mm ²)	70	71	72	66	68	68	72
熱膨張係数 α ₁₀₋₃₀₀ (10 ⁻⁶ /K)	8.2	8.9	9.1	9.6	9.1	9.1	8.9
ガラス遷移温度T _g	595	632	618	565	573	579	626

アルカリ金属の浸出量とは、上述の試験を上述の条件下で行った場合のハードディスク基板1枚あたりのアルカリ金属イオンの総浸出量 (μg) を意味するものである。「応力緩和 (h)」のラインは、一定温度 (300 °C) とした場合に、圧縮応力帯域の厚さが測定可能となるまで減少するのに要した時間 (h) を示す。因みに、4 μm を超す厚さの変化が測定可能である。使用した光学的方法については、すでに説明したとおりである。圧縮応力帯域の厚さのこうした低減は、圧縮応力の低減に関連したものであり、圧縮応力緩和それ自体よりは測定が容易である。 40

【0027】KNO₃ 浴中で、表1の実施例3の組成を有するガラスを化学硬化する間、イオン交換時間を1/2時間から15時間まで変化させ、浴温度を350 °C から550 °C まで変化させた。得られた圧縮応力帯域の厚さ (μm) を表2に示す。圧縮応力帯域の厚さは14 ~ 230 μm の範囲で、温度が低いほど長い浸漬時間が必要である点は、予測通りであった。

【表2】

表1の実施例3の組成を有するガラスについての、イオン交換時間又は塩浴温度の関数としての圧縮応力帯域 (μm)					
イオン交換時間 (h)	浴温度 ($^{\circ}\text{C}$)				
	350	400	450	500	550
0.5		14	20	38	46
1			26	55	68
1.5		20	30	60	90
2.5		31			
4			42		121
5		45		98	
8			75		
10		63	90	132	182
15	47	72	103	166	230

表1の実施例3の組成を有するガラスについての、一定の塩浴温度(450 $^{\circ}\text{C}$)でのイオン交換時間の関数としての圧縮応力帯域の厚さ、表面での圧縮応力、及び曲げ強さ			
イオン交換時間 (h)	圧縮応力帯域の厚さ (μm)	表面での圧縮応力 (N/mm^2)	曲げ強さ (N/mm^2)
1.5	30	880 \pm 30	430
15	103	775 \pm 30	800

上記のような極めて良好な曲げ強さの値を有しているの、本発明の新規な方法によって製造された強化ガラスは、ハードディスクに現在負荷されている、あるいは(将来のハードディスクの高スピードによって)負荷されることになる機械的荷重に耐えるうえで最適のものとなっている。

【0029】上記表1に関連して言及した応力緩和の温度依存性を、表4に示す。この目的で、表1の実施例7※

※の組成を有するガラスから製造したハードディスク基板を、 KNO_3 浴中で、520 $^{\circ}\text{C}$ にて20時間にわたって硬化させた。圧縮応力が800 N/mm^2 の220 μm の圧縮応力帯域が形成された。表4は、各温度で、圧縮応力帯域の厚さの減少が観察されるまでに経過した時間を示す。

【表4】

表1の実施例7の組成を有するガラスについての、所定温度で圧縮応力帯域の厚さに測定可能な減少(4 μm)が生じるまで経過した時間	
温度 ($^{\circ}\text{C}$)	時間 (h)
300	>1000
350	500
400	100
500	30

外押を行うと、200 $^{\circ}\text{C}$ の温度では、応力緩和が生じる50までに50,000時間以上が経過することになる。も

*【0028】このように、圧縮応力帯域の厚さは、イオン交換時間(イオン交換温度が一定の場合)及びイオン交換温度(イオン交換時間が一定の場合)の双方に明らかに依存している。表3は、こうした依存性が、表面での圧縮応力にはそのまま当てはまるものではないが、曲げ強さに関しては確実に当てはまることを示している。この場合も、実施ガラスとして選択したのは、表1の実施例3の組成を有するガラスであった。

【表3】

と著しく低い温度、例えば60℃未満の温度では、圧縮応力は、強度特性とともに、実質的に無限に保持されるとみなすことができる。

【0030】曲げ強さ以外にも、アルカリ金属の浸出量が少ないこと、すなわち耐薬品性が高いことが、この新規な方法によって製造したガラスに特徴的な点である。この特性を具体的に示す目的で、表1の実施例3のガラスにKNO₃浴中で化学強化処理を施すにあたり、強化*

*処理時間及び温度を再度変化させ、そのそれぞれについて、アルカリ金属の浸出量を測定した。結果を表5（イオン交換時間を変化させた場合）及び表6（イオン交換温度を変化させた場合）に示す。各ケースについて3つの試料で浸出させ、浸出量を測定した。表に示す結果は、再現性があった。

【0031】

【表5】

表1の実施例3の組成を有するガラスについての、一定の塩浴温度(450℃)での、強化処理時間の関数としての、ハードディスク基板1枚あたりのアルカリ金属浸出量(μg)			
強化処理時間(h)	浸出量(μg/試料)		
	Na ⁺	K ⁺	ΣNa ⁺ +K ⁺
0	22	3	25
0.5	2	20	22
1.5	2	22	24
2.0	2	22	24
4.0	2	24	26
10.0	3	16	19
15.0	6	8	14

表5の第1行には、強化処理時間が0時間の未強化ガラスを比較例として示してある。浸出したイオンの分布に変動があるのは、強化ガラス及び未強化ガラスの表面での元素分布に違いがあるからである。とはいえ、強化ガラスのアルカリ金属イオンの総浸出量が、化学強化処理を施していないガラスの場合と同程度に低いことは、驚くべきことであると同時に重要である。すなわち、強化*

※処理を行ったにもかかわらず、良好な耐薬品性が保持されているのである。さらに驚くべきは、強化処理時間を延ばしても、アルカリ金属の浸出量がほとんど増えず、それどころか、イオン交換時間が長くなるとアルカリ金属の浸出量が低減することである。

【0032】

【表6】

表1の実施例3の組成を有するガラスについての、一定の強化処理時間(2時間)での、強化処理温度の関数としての、ハードディスク基板1枚あたりのアルカリ金属の浸出量(μg)			
強化処理温度(℃)	浸出量(μg/試料)		
	Na ⁺	K ⁺	ΣNa ⁺ +K ⁺
350	6	22	28
400	2	21	23
450	2	22	24
500	3	20	23
550	3	21	24

表6に示されるように、アルカリ金属の浸出量は、強化処理温度によってほとんど影響を受けない。

【0033】記載通りの組成を有し、記載通りの条件で化学強化処理を行ったガラスは、アルカリ金属浸出量、即ち、耐薬品性を有意に変化させることなく、例えば研

磨によって厚さを相当程度低減させることが可能であることを表7に示す。この表では、表1の実施例3の組成を有するハードディスク基板からのアルカリ金属浸出量を、2つの異なった硬化処理時間について示す。このハードディスク基板は、いずれの場合も、強化処理の前で

なく、強化処理の後に、厚さが10 μ m減少するまで酸化セリウムで両面を研磨したものである。残留荒さは、1nm未満とした。研磨前の圧縮応力帯域の厚さは、3 μ m（強化処理時間、2.5時間）あるいは40 μ m*

*（強化処理時間、3.0時間）であった。表中の値は、3回の測定で確認した。
【表7】

表1の実施例3の組成を有するハードディスク基板に、強化処理温度460℃で、2種の強化処理時間で強化処理を施し、その後、各事例とも、両面を研磨して厚さを10 μ m減少させた場合の、ハードディスク基板1枚あたりのアルカリ金属の浸出量（ μ g）			
強化 処理時間 (h)	浸出量（ μ g/試料）		
	Na ⁺	K ⁺	Σ Na ⁺ + K ⁺
2.5	5	10	15
3.0	5	13	18

この結果から、ここに記載した本発明の特定の実施態様の方法、即ち、強化処理を行った後に研磨を行うという方法が有する利点のはっきりわかる。良好な耐薬品性が

保持され、イオン交換によって損なわれることがあった表面品質が、処理後の研磨によって恒久的に改善されている。

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